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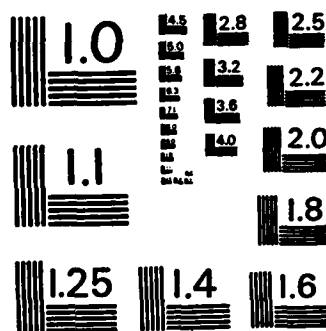


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A NOVEL LIQUID SILAZANE
PRECURSOR TO SILICON NITRIDE

by

Dietmar Seyferth, Gary H. Wiseman
and Christian Prud'homme

Prepared for Publication
in the
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Dietmar Seyferth, Gary H. Wiseman and Christian Prud'homme

SUMMARY

The reaction of dichlorosilane, H_2SiCl_2 , with gaseous ammonia in dichloromethane or diethyl ether solution results in formation of a silazane oil containing silicon, hydrogen and nitrogen in good yield. This ammonolysis product can be pyrolyzed in a nitrogen atmosphere (temperature to 1150°C) to give $\alpha\text{-Si}_3\text{N}_4$ in about 70% yield. The ceramic product formed has a relatively porous, fine-grained microstructure with some cracks and blisters.

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about 70% yield. The ceramic product formed has a relatively porous, fine-grained microstructure with some cracks and blisters.

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INTRODUCTION

The formation of ceramics by the pyrolysis of appropriate polymeric materials has become a research area of increasing interest and importance to both chemists and ceramists, e.g., as indicated by the mini-symposium on this topic at the American Ceramic Society Meeting in 1981.¹ While much of the recent attention has focused on the production of silicon carbide fibers and ceramics by pyrolysis of suitable organosilicon polymers,² the polymer-to-ceramic conversion should be of broad, general applicability. We report here on our application of this procedure to the preparation of silicon nitride, Si_3N_4 .

At present, silicon nitride is prepared primarily by the reaction of elemental silicon with gaseous ^{or ammonia} nitrogen at elevated temperatures to produce either ceramic bodies directly (reaction sintering) or powder for subsequent processing.³ Chemical vapor decomposition procedures, i.e., gas phase, high temperature reactions of ammonia with chlorosilanes, also have been used in the preparation of silicon nitride.⁴ Its excellent chemical inertness, thermal shock resistance and hardness make Si_3N_4 a material of great interest for a variety of applications.³

Although organosilazane polymers, e.g., $[(\text{CH}_3)_2\text{SiNH}]_x$, have been used in the pyrolytic preparation of silicon nitride,⁵ with such precursors which contain organic substituents on the silicon atoms there always is the possibility that the products will contain carbon and/or silicon carbide as well as silicon nitride. Ideally, the polymeric Si_3N_4 precursor should contain only Si, N and, perhaps, other elements which will be completely lost in the gaseous products in the pyrolysis step.

The silicon halide/ammonia system would appear to meet this requirement, and, in fact, the solution reaction of SiCl_4 and ammonia has received considerable study.⁶ A solid, insoluble, cross-linked product, silicon diimide, $[\text{Si}(\text{NH})_2]_x$, results, which is admixed with four molar equivalents of ammonium chloride. This material can be pyrolyzed to $\alpha\text{-Si}_3\text{N}_4$ at 1250°C , but it is of limited utility because of its insolubility. Of substantially greater applicability would be a liquid polysilazane precursor to Si_3N_4 , one which is capable of being infiltrated into the pores of ceramic bodies, of serving as a binder for ceramic powders and fibers, of being used to surface-coat ceramic bodies, and which on pyrolysis gives silicon nitride. This note presents a preliminary report on such a liquid Si_3N_4 precursor.

RESULTS AND DISCUSSION

Early work by Stock and Somieski⁷ showed that dichlorosilane, H_2SiCl_2 , reacts with ammonia in benzene solution to give, after removal of the precipitated ammonia chloride by filtration and, subsequently, the solvent by distillation at reduced pressure, a viscous oil which was not stable at room temperature. During the course of one day it changed to a clear, hard glass. Cryoscopic molecular weight measurements showed that the oil was an oligomeric product with a molecular weight of ~ 350 . This work was not followed up by Stock or by later workers.

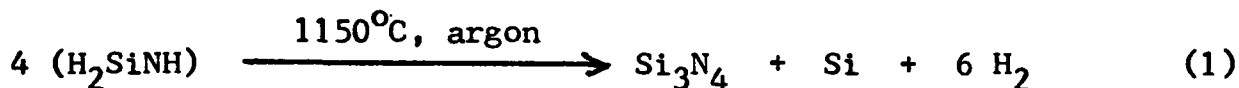
We find that dichlorosilane reacts with gaseous ammonia more readily in polar solvents such as dichloromethane or diethyl ether to give polysilazane oils which on the basis of analysis (Si and N; absence of Cl) and spectroscopy (infrared and proton NMR) appear to deviate from the ideal formula, $[\text{H}_2\text{SiNH}]_x$. The ammonolysis product

can be isolated in good yield from either solvent simply by filtration to remove NH_4Cl and high vacuum distillation of volatiles. The oil which is obtained initially as a nonvolatile residue is not very viscous. (Because of the instability of the Si-N bonds of silazanes toward hydrolysis, all operations must be carried out under a dry nitrogen or argon atmosphere). The oil is stable indefinitely at -30°C in nitrogen-filled vials, but at room temperature its viscosity increases gradually; after 3-5 days a glassy solid has formed, without significant weight loss. The deviation from "ideal" composition is believed to be due to the operation of cross-linking processes. The 250 MHz proton NMR spectrum of the oil showed two complex multiplets at δ 4.3 and 4.7 ppm due to Si-H protons and a broad resonance between 1.0 and 1.7 ppm which is assigned to N-H protons, with an Si-H/N-H area ratio of 3.3. The infrared spectrum of the oil showed only one peak in the N-H stretching region at 3390 cm^{-1} (indicating the presence of NH but not of NH_2), as well as bands at 2172 (ν Si-H), 1180 (δ N-H) and 1020-840 (δ Si-N-Si). Of importance is the fact that there were no bands in the $1150\text{-}1000\text{ cm}^{-1}$ region (Si-O-Si). Further work aimed at elucidating the structure of this ammonolysis product is in progress.

The decomposition of the oil produced in the solution ammonolysis of dichlorosilane was studied by thermogravimetric analysis (TGA). At a constant heating rate of $1.0^\circ\text{C}/\text{min}$ (from room temperature to 1200°C) the decomposition proceeded smoothly and asymptotically with no inflections in the weight loss vs temperature graph (Fig. 1). The onset of weight loss occurred at about 50°C and weight loss was virtually complete at 450°C , amounting to 31% of the initial weight. The final product was a black solid. The composition of the volatile products formed in the pyrolysis is under investigation. Since the loss only

of H_2 from the "ideal" composition, $(H_2SiNH)_x$, corresponds to a weight loss of only 6.7%, the decomposition process clearly is more complex.

In our designed formation of ceramic materials, the oil which was obtained as the initial ammonolysis product of H_2SiCl_2 , in a fused silica boat, was heated to $200^\circ C$ in a quartz pyrolysis tube under a slow flow of argon for 1 h. This treatment resulted in solidification of the sample. Subsequently, the temperature was increased slowly to $1150^\circ C$ and maintained at this temperature for 5 h. A brown, crystalline solid was produced which was identified as a mixture of α - Si_3N_4 ,⁸ β - Si_3N_4 ⁸ and elemental silicon⁹ on the basis of its X-ray powder diffraction pattern. Eq 1 shows this process for the "ideal" composition; the formation of elemental silicon thus is to be expected. If the pyrolysis of the ammonolysis product was con-



ducted in a stream of nitrogen (12 h at $1150^\circ C$), the X-ray diffraction pattern of the brown solid obtained showed the presence of α - Si_3N_4 and of only a trace of elemental silicon.

At this early stage, formation of bulk bodies has not been sought. However, ready production of solid pieces with dimensions of 1 to a few mm seem encouraging. Such pieces allowed measurement of immersion densities of 2.5 g/cc and open porosities $> 10\%$. Scanning electron microscopy (SEM) examination of pieces of the pyrolysis products showed some cracking and blistering of the solid, probably due, respectively, to shrinkage and gas release during pyrolysis (Fig.2). Crack spacings on the order of 20-30 μm indicate that the formation of small (1-10 μm) crack-free fibers from the ammonolysis product should be quite feasible. The SEM micrographs also show a fine grain

structure ($\sim 0.2 \mu\text{m}$), suggesting that fibers or bodies from this polymer-derived Si_3N_4 could show good mechanical properties (Fig. 3).

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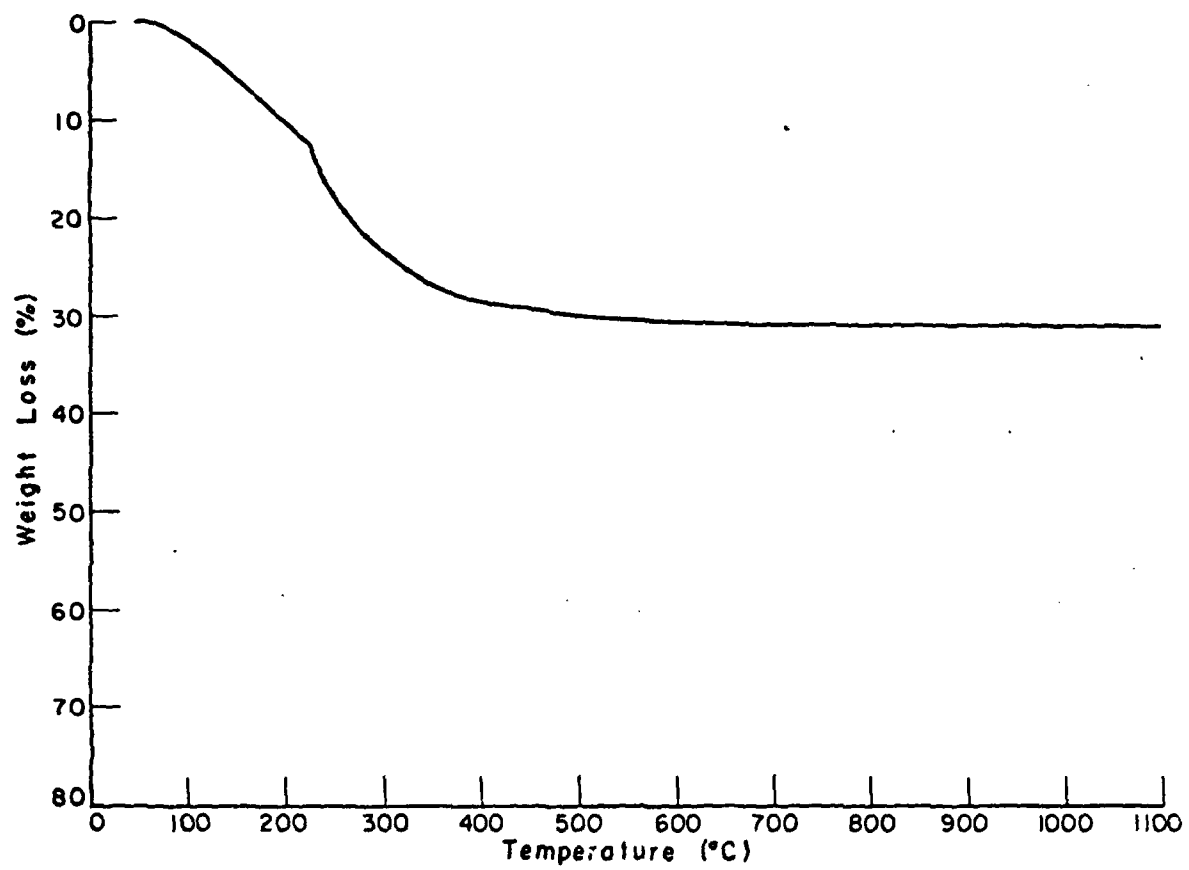
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FIGURE CAPTIONS

Fig. 1 TGA of Dichlorosilane
Ammolysis Product

Fig. 2 SEM Micrograph of Pyrolysis
Product of H_2SiCl_2 -Derived
Polysilazane (3h, 1200°C,
under nitrogen)
(a) 4X (b) 40X

Fig. 3 SEM Micrograph of Pyrolysis
Product of H_2SiCl_2 -Derived
Polysilazane (3h, 1200°C,
(a) 1KX (b) 2.8KX







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